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The Capacity of the Capillary Electrometer

By A. L. CLARK, Ph.D., F.R.S.C.

(Read May Meeting, 1920)

In spite of the fact that the capillary electrometer has been the subject of study ever since the pioneer work of Lippmann[1], the question of the cause of the large capacity and its possible variation with the potential difference cannot be said to have been answered satisfactorily. The controversy over the explanation of electro-capillary phenomena and the existence of an electric double layer at the boundary between a metal and an electrolyte or a gas is still open to contribution and the importance of the question makes advisable the publication of the following investigation.

If the large capacity of the electrometer is due to a double layer such as conceived by Helmholtz,[2] it might be expected that the properties of this double layer would depend on the difference of potential of the two sides and the capacity[3] might be a function of this potential difference. Contrary to the explicit statement of Burch[4] that the capacity is independent of the difference of potential, preliminary observations showed that the capacity is a function of the potential difference. Also, contrary to his statement of the case, the capacity is very different when the direction of the applied potential is reversed. As ordinarily used, the mercury of the electrometer is the cathode. Otherwise the mercury becomes fouled after a short time and sticking results. Later study of the variations of capacity have confirmed the results obtained earlier, and the following paper is an account of the work carried out in the summer of 1917.

APPARATUS

The form of electrometer used is essentially the same as that used by Burch with a few modifications for convenience in handling and for changing capillaries. The tubing was of the soft, soda-glass variety selected to be free from irrgeularities. It was washed with hot aqua-regia, water, hot potassium hydroxide and distilled water and finally

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[1] Lippmann, Pogg. Ann. 149, 546, 1873; Wied. Ann. II, 320, 1880. Compt. rend. 76, 1407, 1873; 95, 686, 1892. Ann. de Chem. et Phys. (5), 494, 1877; Jour. de Phys. (2) 2, 116, 1883.

[2] Helmholtz. Wied. Ann. 7, 337, 1879; 16, 30, 1882.

[3] The word capacity is used here in the sense of apparent capacity.

[4] Burch, Electrician (London). July 17, 27, 31, Aug. 7, 1897.

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with re-distilled water. The tubes were dried by a current of air, drawn through a drying train to ensure freedom from dust. Too great care in washing cannot be exercised if smooth action is desired.

The mercury was washed in dilute nitric acid and distilled. After the first distillation, the still was carefully cleaned and the mercury re-distilled into the electrometer tubes as needed. The electrolyte for the major part of the work was 25 per cent sulphuric acid. The platinum wires for connecting to the mercury in the electrometer were carefully cleaned before inserting and all points in the connecting tubing were either welded or they were sealed with wax in the case of glass-rubber connections. If carefully prepared, there is no sign of any leakage of air from the apparatus, practically no leakage of charge, no trace of local emf. when on closed circuit, or creeping on open circuit.

For charging the electrometer, a simple potentiometer consisting of a stretched nichrome wire provided with sharp-edged moveable contacts, was used. This potentiometer wire was connected in series with a rheostat, a milammeter and a storage cell. The wire itself was carefully tested and found to be uniform and the contacts were without appreciable resistance. The latter point is very important for low potentials, as any irregularity in contact leads to incorrect values of the capacity.

The excursions of the electrometer were measured with a micrometer microscope mounted on a micrometer slide.

Capacity Measurements

Since the capacity of any electrometer depends on the position of the meniscus in the tube, all observations of the capacity for purposes of comparison must be made at the same point in the tube. The capacity can be measured by the method of mixtures using the electrometer itself instead of a galvanometer, but a better method is to charge a standard condenser to a known potential and allow it to share its charge with the uncharged electrometer. The condenser is charged to the desired P.D. which is known from the potentiometer to which it is connected. Next, the condenser is insulated from the source of supply and connected to the electrometer. The excursion of the meniscus is noted and then a second connection to the potentiometer gives the P.D. after the mixture. When the condenser is charged to a new P.D. the position of the meniscus is adjusted by changing the pressure so that the meniscus always comes to rest at the same point in the tube throughout the series.

The method of charging the electrometer and allowing it to share its charge with a standard condenser is not satisfactory owing to the change in capacity of the electrometer due to the changed position of the meniscus.

If the original potential of the standard condenser of capacity C_1 is V_1 and after mixture is V, we have for the total charge

$$Q_1 = C_1V_1 = (C_1 + C)\ V = C_1V + Q$$

where C is the capacity of the electrometer in the final position. Q is the charge in the electrometer after mixture. From these equations

$$C = C_1 \frac{V_1 - V}{V}$$

$$\text{or} \qquad Q = C_1\,(V_1 - V).$$

Using the first we may get the value of C, but for comparison of results, we may plot Q against V, *i.e.*, the charge in the electrometer against the potential. Then, if the capacity is constant the graph will be straight, if variable it will be curved.

If the capacity is not constant it should be defined as $\frac{dQ}{dV}$, or as the slope of the Q-V curve. The ordinary definition of capacity at any given potential difference gives the average value over the interval of potential from zero to the final value.

Figure 1 shows the general character of the results of capacity measurement. In most cases for direct charging, with mercury as the cathode, the capacity decreases as the potential difference increases and becomes nearly constant. For reverse charging the capacity always increases and for the larger potentials becomes very large. The slope of the curve is continuous through the origin. In a few cases, the curve for direct charging was concave upward and the capacity increased a little and became constant. In either case the capacity seems to approach a steady value. In all cases where the curve for direct charge is concave upward, the capacity is very high. This form of curve is easily interpreted.

We may regard the electrometer as a system composed of two condensers in series, one at the surface of the mercury in the capillary tube, the other at the surface in the larger vessel. If we call the capacity of the first C_1 and that of the second C_2, the combined capacity is given by

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad \text{or}$$

$$C = \frac{C_1C_2}{C_1 + C_2}$$

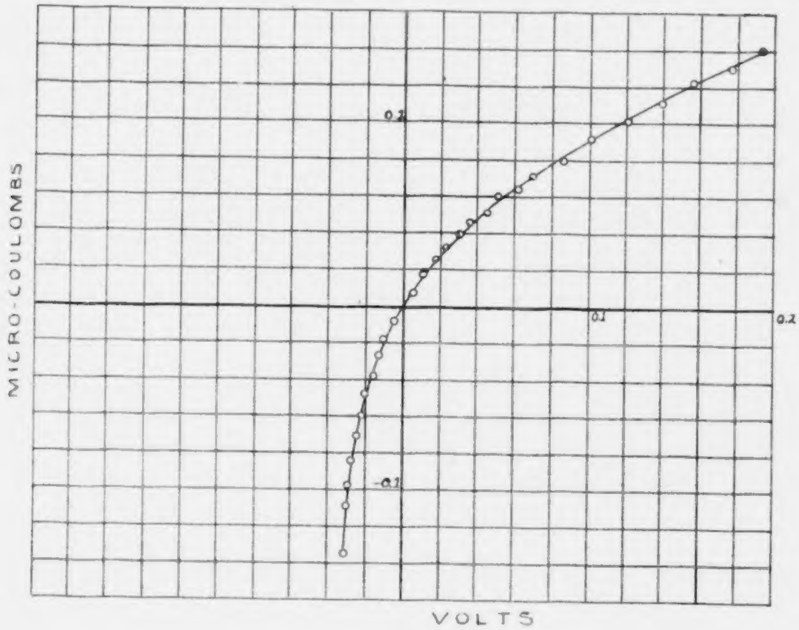

FIG. 1.

If C_2 is very large compared with C_1, this becomes $C=C_1$ and the apparent capacity is that of the smaller condenser. If C_1 is not sufficiently small, then C depends on C_2.

If we add a small charge, dq, to the electrometer, the capacity changes by the amount

$$d\,C = \frac{C_1^2 dC_2 + C_2^2 dC_1}{(C_1+C_2)^2}$$

So the change in observed capacity depends on $C_1^2dC_2+C_2^2dC_1$.

In many of the observed cases dC_1 is negative, while dC_2 is always positive. If we assume that this is always true, then C may increase, decrease or remain stationary if $C_1^2dC_2-C_2^2dC_1$ is greater than, less than, or equal to 0 respectively, or if $\frac{dC_2}{dC_1}$ is greater than, less than, or equal to $\frac{C_2^2}{C_1^2}$.

Examination of Figure 1 (which is for the case where C_2 is very large compared with C_1 and hence $C=C_1$) we see that the changes in capacity for negative charging are very large compared with those with positive charging. The same must be true for C_2. Hence $\frac{dC_2}{dC_1}$ will be very large, as the slope of the tangent in the negative part of the curve changes very rapidly. So in case $\frac{C_2^2}{C_1^2}$ is not very large, we may have $\frac{dC_2}{dC_1} > \frac{C_2^2}{C_1^2}$ and then $dC > 0$ and the curve slopes upward in the positive portion.

In case $\frac{C_2}{C_1}$ is very large the curve will slope as in Figure 1.

Since in making these determinations of capacity, it is necessary to have the meniscus stop at the same point after the discharge into the standard condenser, the pressure requires adjustment to bring the meniscus to the proper final point. While it seemed unlikely that this small change of pressure would have any effect on the capacity, an electrometer was arranged to be placed inside a bell jar from which the air could be removed. This necessitated an arrangement for a wide change of pressure, which was accomplished without much difficulty. There is certainly no change in capacity due to change of pressure of an amount less than one atmosphere.

A striking example of the increase of capacity with negative charging of the electrometer was seen in the case of electrical oscillations of a system in which the electrometer was included. All attempts to build an electrometer with resistance low enough to obtain oscillations[1] with it in series with a self-inductance proved futile. But, by arranging a standard condenser in parallel with the electrometer and these in series with the self-inductance, oscillations are possible. Approximate theory shows that these are oscillations impressed on a logarithmic charge or discharge curve.

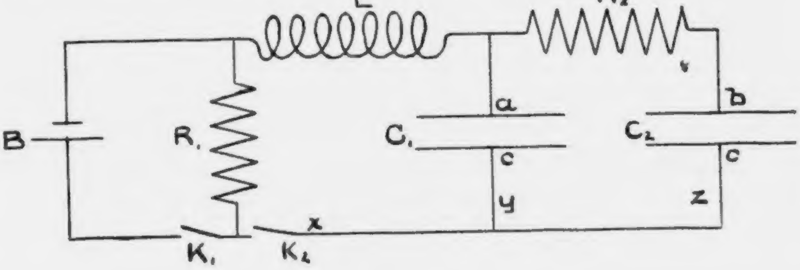

FIG. 2.

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[1] In a later paper an oscillatory system will be described where the capacity is that of a pair of polarized electrodes.

We may treat the electrometer as though it were a simple condenser in series with a high resistance, neglecting both changes in this resistance and the capacity of the condenser. The arrangement of the discharge circuit is shown in Figure 2. The battery whose emf is E supplies the current I through the resistance R_1 and a key K_1, which is one of the keys of a drop chronograph. The two condensers of capacities C_1 and C_2 are connected as shown and are charged so that the potential difference is I R. R_2 is the high resistance of the electrometer whose capacity is C_2. L is a self-inductance inserted so that the discharge may be oscillatory. The second key K_2 of the drop chronograph may be inserted at x, y or z. When both keys are closed the system is charged and in both condensers the plates are at a common difference of potential I R. If K_1 is opened the discharge begins and continues until K_2 is opened. If K_2 is at x, the oscillation ceases and the two condensers settle down to the same difference of potential. If K_2 is at y, the first condenser C_1 is left with the charge it had at the instant of opening the key K_2. If K_2 be connected at z, the condenser C_2 is left with the charge it had at the instant of opening the key. In any case we may measure the charge by connecting both with a ballistic galvanometer and calculate the potential from the known capacities. Or we may connect to an electrometer and measure the potential. For the case where K_2 is at x or z, we may use the capillary electrometer to measure the potential. The first arrangement only was used.

Suppose plates *a* and *b* are charged positively so that when K_1 is opened the charge flows from *a* and *b* through the system. Let the current in circuit 1 be i_1, in circuit 2 be i_2, the charge on plate *a* of C_1 be q_1, on plate *b* of C_2 be q_2, potential of *a* be V_a and of *c* be V_c. Let R_1 include resistance of L. We may call the capacities of the condensers C_1 and C_2 respectively.

Then:

$$i_1 R_1 = V_a - V_c - L\frac{di_1}{dt} = \frac{q_1}{C_1} - L\frac{di_1}{dt}$$

$$i_2 R_2 = V_b - V_a = V_b - V_c - (V_a - V_c) = \frac{q_2}{C_2} - \frac{q_1}{C_1}$$

and also,

$$i_2 = -\frac{dq_2}{dt} \text{ and } i_1 = -\frac{dq_1}{dt} - \frac{dq_2}{dt}$$

So we have
$$L\left(\frac{d^2q_1}{dt^2} + \frac{d^2q_2}{dt^2}\right) + R_1\left(\frac{dq_1}{dt} + \frac{dq_2}{dt}\right) + \frac{q_1}{C_1} = 0 \qquad (1)$$

and
$$R_2\frac{dq_2}{dt} + \frac{q_2}{C_2} - \frac{q_1}{C_1} = 0 \qquad (2)$$

$$\text{or} \quad q_1 = \frac{C_1 q_2}{C_2} + C_1 R_2 \frac{dq_2}{dt}$$

We may differentiate this equation and substitute in (1), obtaining

$$\frac{d^3q_2}{dt^2} + \frac{C_1R_1R_2 + L + \frac{LC_1}{C_2}}{L\,C_1\,R_2}\frac{d^2q_2}{dt^2} + \frac{R_1 + R_2 + R_1\frac{C_1}{C_2}}{L\,C_1\,R_2}\frac{dq_2}{dt} + \frac{q_2}{LC_1C_2R_2} = 0 \tag{3}$$

We may apply the general method for linear differential equations with constant co-efficients by placing $q_2 = \epsilon^{\lambda t}$, substitution of which in (3) gives

$$\lambda^3 + \frac{C_1R_1R_2 + L + L\frac{C_1}{C_2}}{L\,C_1\,R_2}\lambda^2 + \frac{R_1 + R_2 + R_1\frac{C_1}{C_2}}{L\,C_1\,R_2}\lambda + \frac{1}{L\,C_1\,C_2\,R_2} = 0 \tag{4}$$

yielding three values of λ, so that

$$q_2 = a_1\epsilon^{\lambda_1 t} + a_2\,\epsilon^{\lambda_2 t} + a_3\epsilon^{\lambda_3 t} \tag{5}$$

It will be shown later that only one root of the λ equation is real. The other two must be conjugate imaginaries. We may call $\lambda_1 = \lambda$, the real root, and the other two may be written $\alpha + i\beta$ and $\alpha - i\beta$. So we have finally

$$q_2 = a\epsilon^{\lambda t} + \epsilon^{\alpha t}\,(A\cos\beta t + B\sin\beta t) \tag{6}$$

Differentiation and substitution in (2) give

$$q_1 = a\left(\frac{C_1}{C_2} + C_1R_2\,\lambda\right)\epsilon^{\lambda t} \tag{7}$$

$$+\,\epsilon^{\alpha t}\left[\left\{\frac{C_1}{C_2}A + C_1R_2(A\alpha + B\beta)\right\}\cos\beta t + \left\{\frac{C_1}{C_2}B + C_1R_2(B\alpha - A\beta)\right\}\sin\beta t\right]$$

We may, of course, write (6) as

$$q_2 = a\epsilon^{\lambda t} + A\epsilon^{\alpha t}\cos\,(\beta t - \phi) \tag{8}$$

$$\text{where} \quad A = \sqrt{A^2 + B^2} \ \text{and} \ \phi = \tan^{-1}\frac{B}{A} \tag{9}$$

and in the same manner

$$q_1 = \left(\frac{C_1}{C_2} + C_1R_2\,\lambda\right) a\,e^{\lambda t} + A_1\,e^{\alpha t}\cos\,(\beta t - \phi + \omega) \tag{10}$$

$$\text{where} \qquad A_1 = A\sqrt{\left(\frac{C_1}{C_2} + C_1\,R_2\,\alpha\right)^2 + C_1^2\,R_2^2\,\beta^2}$$

$$\text{and} \quad \omega = \tan^{-1}\frac{C_2\,R_2\,\beta}{1 - C_2\,R_2\,\alpha} \tag{11}$$

ω is the difference in phase of the two discharges. It will be noticed that both discharges are oscillatory and consist in each case of a damped oscillation impressed upon an exponential discharge.

In the experimental determination of the discharge curve the following values were used:

$C_1 = 10^{-6}$ farad.
$C_2 = \cdot 27\ (10)^{-6}$ farad (capillary No. 12).
$L = \cdot 81$ henries.
$R_1 = 100$ ohm.
$R_2 = 171000$ ohm (capillary No. 12, approximate value).

C_2 was measured by the method already outlined and is the value for zero difference in potential. The resistance was determined from the discharge curve as explained later.

The λ equation becomes

$$\lambda^3 + 150{,}\,3\lambda^2 + 1{,}238{,}700\,\lambda + 26{,}741{,}000 = 0 \qquad (12)$$

Trial shews one root to be $-21\cdot 64$, and the resulting equation yields the roots $-64\cdot 33 \pm 1110\,i$ (13)

so that $\alpha = -64\cdot 33 \qquad \beta = 1110.$

and the period $\dfrac{2\pi}{\beta} = \cdot 00566.$

The period obtained by experiment is $\cdot 00567$ sec.

We may now determine the constants of integration,

for when $t = 0\ \ q_2 = Q_2,\ \dfrac{dq_2}{dt} = 0,\ \ q_1 = Q_1$ and $\dfrac{dq_1}{dt} = 0$

of which one is redundant.

Take $a + A = Q_2$

$$a\,\lambda + \alpha\,A + \beta\,B = 0. \text{ and}$$

$$a\,\lambda^2 + \alpha^2\,A + 2\,\alpha\,\beta\,B - \beta^2\,A = 0$$

Solving and substituting values, we have

$$\left.\begin{aligned} a &= 1\cdot 00188\,Q_2 \\ A &= -\theta\cdot 00188\,Q_2 \\ B &= 0\cdot 0194\,Q_2 \end{aligned}\right\} \qquad (14)$$

and $\phi = \tan^{-1} 10\cdot 32 = -84^0\cdot 28^1$
$\omega = \tan^{-1} 23\cdot 93 = 87^0\ 48^1$
$\phi^1 = \tan^{-1} \cdot 05816 = 3_1{}^0 19$

We may obtain q_2 experimentally by inserting K_2 at z, q_1 by inserting at y and q_1+q_2 by inserting at x (Fig. 2)

Since $Q_2 = \dfrac{C_2}{C_1}\,Q_1 = .\cdot 27 Q_1$

$$q_1+q_2 = Q_1\left\{\cdot 2715\,\epsilon^{-21\cdot 64t} + \epsilon^{-64\cdot 33t}\begin{pmatrix}\cdot 9938\cos 1110t + \cdot 0633 \\ \sin 1110t\end{pmatrix}\right. \qquad (15)$$

If we use the capillary electrometer to indicate the potential without determining q_1 or q_2, we may insert key K_2 at either z or x, when we obtain the potential of the electrometer at the instant of opening K_2, or we may obtain the final potential of the system when it settles down after K_2 is opened.

Using $E_1 = \frac{q_1}{C_1}$ and $E_2 = \frac{q_2}{C_2}$

we have the potential of the condenser system at any instant

$$E = \frac{q_1+q_2}{C_1+C_2} = \frac{C_1 E_1}{C_1 + C_2} \left\{ \cdot 2715, \text{ etc.} \right. \tag{16}$$

This equation plotted follows the general character of the experimental curve, but the amplitude is considerably greater. This is to be accounted for, probably in the emf of the concentration cell caused by the transport of ions in the acid solution due to the passage of electricity through it.

For making or breaking the circuit in this and other determinations of charge and discharge curves a Webster chronograph[1] was used. The potentiometer connections were led to a non-inductive resistance through one key of the chronograph. The self-inductance (·81 henries), and the electrometer and condenser in parallel, were connected to the terminals of the non-inductive resistances through the second key of the chronograph. The falling weight opens the two

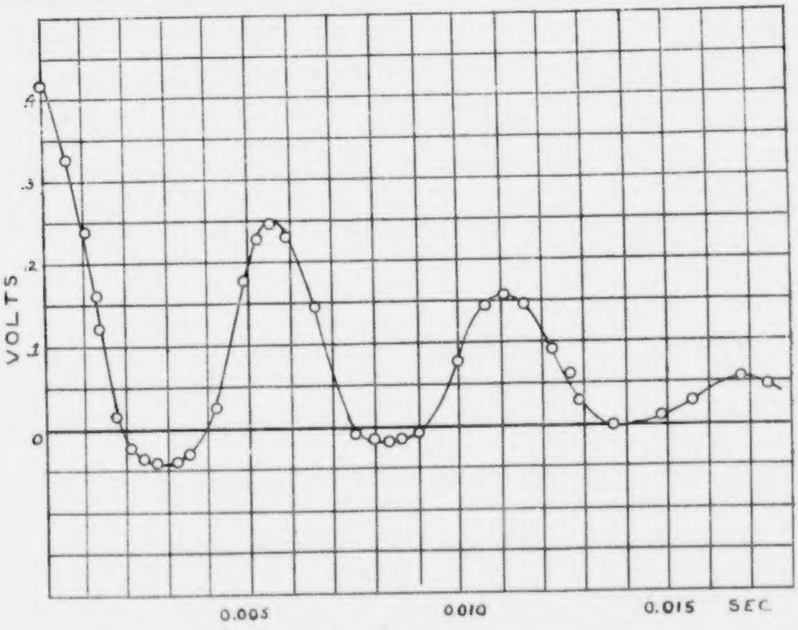

FIG 3

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[1] Webster. Physical Review (I), VI, 297, 1898.

keys with a short interval of time between and the electrometer shows the final potential of the condenser. This time interval may be changed at will over a wide range and a series of readings taken for different times of charge or discharge.

Figure 3 shows the result using for $R = 100$ ohms. The standard condenser had a capacity of 1 microfarad and the electrometer about ·27 microfarads with normal charging.

It will be noticed that the minima are much nearer the mean positions on which would be a logarithmic curve than the maxima, and the curvature is much less also. This is the result of the condenser having different capacities in the different directions.

NON-OSCILLATORY DISCHARGE CURVES

It was easy to obtain charge and discharge curves with the above mentioned chronograph, but the effects of varying resistance and capacity are best seen by plotting the results semi-logarithmically. If the resistance of the electrometer is mainly that of the mercury and acid column in the small tube, the changes will be relatively small when the meniscus is not too near the open end of the tube, but may be large if the meniscus is near the end. In the first case, the discharge curve is represented well by $V = V_0\, \epsilon^{-\frac{t}{RC}}$ and the semi-logarithmic plot is straight. On the other hand, if the meniscus is near the end the resistance of the column depends on the position of the meniscus, thus on the potential difference V. We may treat the resistance as though made up of two parts, one approximately constant, and the other approximately proportional to V, so $R = aV + b$ and the current at any instant is

$$i = \frac{V}{aV + b} = -\frac{dq}{dt} = -C\frac{dV}{dt}$$

which is satisfied by

$$Ca\,(V - V_0) + Cb \log\frac{V}{V_0} = -t.$$

Both of these equations are well satisfied by observations taken under the proper circumstances.

Since the capacity increases a little with the increase of potential difference the effect on the discharge curve is of the same general nature as that of the increase in resistance, so all curves plotted as described show a slight curvature.

EXTENT OF THE DOUBLE LAYER

The capacity increases as the meniscus is operated nearer the end of the tube, which is contrary to what might be expected. This fact alone suggests that the double layer is not confined to the meniscus.

Lippmann[1] calculated the thickness of the double layer from observations on the surface tension and the corresponding potential difference which give the surface density σ. The thickness of the double layer is then found from $\sigma = \frac{1}{4\pi d}$.

The calculated value is $d = 1 \cdot 4\ (10)^{-7}$mm. — of *molecular* dimensions. If we calculate the thickness of the double layer from the capacity and the dimensions of the meniscus, we obtain a very much smaller value, *i.e.*, of the order 10^{-12}mm. Then, either the double layer has no such existence, as assumed by Lippmann, or the acid-mercury surface is much greater than the area of the nearly hemispherical meniscus. For example, the capacity of capillary No. 6 was measured in the usual manner and found to be approximately ·25 mf. The diameter of the tube was about ·035 mm. The area of the meniscus is then approximately $2(10)^{-5}$ sq. cm. Then, either the double layer is only $6.8(10)^{-12}$cm. thick or its area is 0·039 sq. cm.

This raises the question of the creeping of the acid solution between the glass and mercury. To test this point, a fresh capillary was drawn (No. 11) and operated as follows: The large tube, which tapered below into the capillary, was filled with mercury in the usual manner. Then it was immersed in the acid and the mercury forced to run out under pressure to exclude air. Then the pressure was reduced gradually until the acid entered the tube a distance of only 2·75 mm. and the capacity was measured at a point 2·5 cm. from the end. Next, the acid was allowed to wet the tube for a distance of 3·00 mm. and the capacity again measured at a point 2·5 mm. and so on. The following values of potentials show that the progressive wetting of the tube with acid does not change the capacity.

Amount wet	Capacity in terms of Potentiometer wire
2·75 mm.	4·68
3·00	4·64
3·25	4·75
3·50	4·89
3·75	4·68

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[1] Lippmann. Compt. rend. 95, 686, 1882.

Then either the acid solution is forced back by the return of the meniscus after wetting, which is not at all likely, or it creeps up of itself between the acid and mercury.

In a paper on the Angle of Contact[1] it was shown that when the angle of contact made with glass by a mercury surface covered with dilute sulphuric acid is zero, the acid creeps between the mercury and glass. Further experiments show that this creep always occurs with H_2SO_4 at least when the concentration is higher than one-half of one per cent. A large number of tubes was prepared by washing with aqua regia, water, potassium hydrate and distilled water. Distilled mercury was placed in the tubes and covered with dilute sulphuric acid. Many different sizes of tubes were used in order to study a possible effect depending on the diameter of the tube. While the smaller tubes seem to have a larger creep than the larger ones, the occurrence of rapid creep among the large and of small creep among the small tubes render such a conclusion doubtful.

The curves for the creep plotted as total distance against the time are approximately exponential. The acid creeps rapidly during the first few hours and then more and more slowly until it becomes almost stationary. Its rate depends so much on the cleanliness of the glass surface that the line between the wetted and unwetted portion, which is very sharp and distinct at first, becomes less and less distinct until it is difficult to follow. Some have been followed for several weeks. Measurements of the electrostatic capacity of these layers show that with constant potential difference the capacity is probably proportional to the area.

Further, the rate of creep depends on the pressure, so that as the acid descends in the tube it reaches regions of greater and greater pressure, so that the motion is slower and slower. If we take a tube small enough to make it possible to invert it without the mercury escaping, the creep is very rapid, in some cases so rapid that it is difficult to follow.

It is easy then to account for the high value of the capacity of the electrometer as used in the above experiments. The acid rises rapidly for some distance in the tube and the wetted area in the conical tube is many thousand times the area of the meniscus.

Experiments show that if the mercury in the tube is the cathode, the rate of creep is diminished by a potential difference applied to the electrometer and increased if the mercury is the anode. But these effects are small and do not explain the changes in capacities observed.

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[1] Clark. Trans. Roy. Soc. Can., XII, 51, 1918.

Measurements of capacity in tubes large enough to permit the measurement of wetted area yield a calculated thickness of the double layer substantially the same as that given by Lippmann.

If we admit the existence of a double layer, the change in capacity with the applied difference of potential seems to indicate a change in the thickness in the double layer brought about by the charges on the plates of the layer.

In conclusion, I have to thank Mr. A. L. Greenlees for his painstaking care in carrying out nearly all of the experimental work in the foregoing paper.

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